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METALLURGICAL ASPECTS OF HEAVY WALL - HIGH STRENGTH SEAMLESS PIPES FOR DEEP WATER APPLICATIONS

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Abstract

The metallurgical design of X65/X70 grade weldable steel flowlines and risers, with a wall thickness greater than 35 mm for deep water, was performed throughout metallurgical modeling, laboratory tests, pilot and industrial trials and advanced metallographic examinations. The role of micro-precipitates in controlling austenite grain growth and the effect of prior austenite grain size (PAGS) and alloying additions on phase transformation during quenching were investigated. The target microstructure in the as-quenched condition was identified as a matrix of refined bainite and low-C martensite with small, well dispersed, islands of MA constituent. This is achieved through fine AGS and very effective quenching. Complex aggregates of high (packets) and low-angle (cells) units and precipitation hardening resulted after tempering. Small packets lead to better low temperature toughness. An optimized chemistry, with proper combination of elements such as Ni, Cr, Mo, Nb and V, and suitable quenching and tempering conditions were identified for pipes of wall thickness up to 42 mm. Addition of 0.20-0.25%Cr produces further improvement in strength, without reducing toughness. Seamless pipes produced by this metallurgical design exhibited suitable mechanical properties at room and high temperature (130 °C), hardness values lower than 248 HV_{10}, and good CTOD values up to – 40 °C of both base metal and HAZ.

1. Introduction

Technology and offshore industry have evolved to meet numerous challenges, *e.g.* deep water, high currents, high pressure and high temperature (HPHT), and sour reservoirs, facing deepwater exploration. The technological evolution in the offshore sector exhibits a trend towards an increasing use of high strength steels both for risers and flowlines. This trend is supported both by economical and technical reasons, because the development of deepwater oil and gas reserves is continuously facing the challenge of containing/reducing costs in all components, as reported by Cook (2002) and Eigbe (2002). On the other hand, wall thickness (WT) is increasing to provide sufficient resistance for the very high operating pressures. The trend in flowline specifications for deepwater offshore fields is a consequence of complex oil-gas field conditions, such as HPHT and developments in design criteria (*i.e.* limit state design), welding and laying technologies. Often the requirements are close to the manufacturing limit of welded pipes, therefore seamless pipes that allow a higher WT/OD are preferred.

As a matter of fact pipe manufacturers are facing new challenges coming from new and/or more demanding material requirements, often related to specific performances and applications, including sour service which set limitations such as maximum material hardness (HV $\leq$ 248).

During the past years technologies have been developed in the field of quenched and tempered (Q&T) seamless pipes. In particular, the heat treatment capabilities of heavy wall pipes have been improved through the introduction of external and internal water quenching, which decreases the through-thickness temperature gradient. Modern seamless pipes are suitable for HPHT applications, provided a proper metallurgical design and processing route are set-up.

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For heavy wall pipes (O.D. = 304.5 mm, WT = 34 mm), a Mo-V steel was selected in order to achieve an adequate combination of strength, yield to tensile ratio (Y/T) and work hardening ratio, even at high temperatures (130 – 160 °C). Such Q&T seamless pipes, which also showed good resistance to strain aging and HIC, were successfully delivered for HPHT offshore production lines, as indicated by Anelli et al. (2001).

When wall pipe was thicker than 34 mm, the required strength (grade X65) could be achieved by the increase of V content (up to 0.1%), but high toughness levels could not be obtained. Therefore, new solutions which are outside of the conventional pattern for (micro)-alloying additions followed so far for Q&T seamless pipes, have to be found for high performance heavy wall X65–X70 seamless pipes throughout a more systematic work.

In this paper, a description is given of the results of fundamental studies on high-strength heavy-wall steel materials manufactured by Q&T processing. This work is part of an on-going development program on high performance Q&T seamless pipes for special deep-water applications, involving metallurgical modeling, laboratory tests, pilot and industrial trials and advanced metallographic examinations. Preliminary results have been reported by Gonzalez et al. (2004) and Anelli et al. (2004). This work has led to a huge number of individual results which called for a complex metallurgical and metallographic evaluation. The most recent findings and overall conclusions are reported hereafter, especially the role of microstructure and precipitation on strength and toughness. These results have been exploited for the production of sour service grade API 5L X65/X70 for flowlines and production risers with WT from 30 mm up to 44 mm for deepwater offshore fields.

2. Metallurgical Background and Modeling

Seamless pipes of medium O.D., *i.e.* up to 406 mm (16") are presently produced by a hot rolling process carried out in the following main stages: hot piercing, hot rolling at retained mandrel mill and sizing. Internal and external quenching, and subsequent tempering, are performed on the pipes in order to refine the microstructure and obtain the required properties.

A rational approach to the design and production of these materials requires the quantitative knowledge of the effects of steel chemistry and heat treatment variables on the microstructure and final mechanical properties. The influence of microalloying additions and Q&T practices on austenite refinement, phase transformation and response to heat treatments of low-C steels for seamless linepipes was investigated by dilatometry and pilot trials. Also an integrated model, containing a thermal routine for simulating pipe quenching, based on the integration by finite differences of the general Fourier heat equation, coupled with a microstructural model, was applied for the design of both the chemical composition and Q&T conditions of seamless pipes. The thermal-metallurgical model is able to calculate the fraction of microstructural constituents and hardness of a steel subjected to rapid continuous cooling after austenitisation (*i.e.* quenching). The calculation is carried out by an Artificial Neural Network (ANN) trained on a selected database of CCT diagrams of linepipe steels (Di Nunzio et al. (2001), Anelli et al. (2003)). The program is able also to simulate a subsequent tempering treatment, predicting hardness (HV), yield strength (YS) and ultimate tensile strength (UTS).

The application of the mathematical model, showed in detail elsewhere (Gonzalez et al. (2004)), indicates that in order to attain the required yield strength for grade X65 in the case of 40 mm WT it is necessary to have a microstructure mainly constituted of a mixture of bainite and low-C martensite, with a fraction of polygonal ferrite below 30% (Figure 1). In order to reach this goal a proper combination of C, Mn, Cr, Mo and Ni is needed.

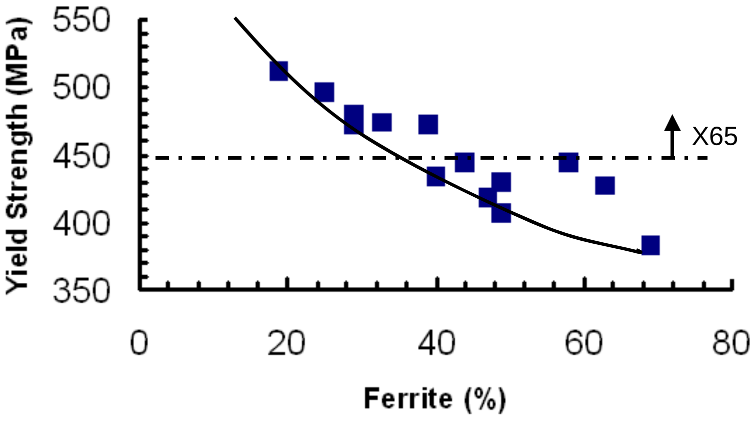


Figure 1. Calculated effect of polygonal ferrite amount on YS of Q&T materials (tempering at 660 °C for 60 min)

The model is an effective tool in defining the optimum chemical composition and Q&T treatments for a given steel to match the required tensile properties of the final product. However, because no information on toughness is available from modeling, a specific experimental activity was carried out to assess the effect of microstructure and precipitation on strength-toughness combination, starting from a promising chemical composition identified by the metallurgical model.

3. Experimental

3.1 Laboratory Tests and Pilot Trials

A series of laboratory heats, with designed changes in the content of Mo, Ni, Cr, V and C, with respect to a base steel composition, were vacuum cast as 80 kg ingots. The carbon equivalent, $C_{eq\ (IIW)}$ was in the range 0.33% to 0.43% and maximum P_{cm} parameter was 0.25%. The ingots were hot rolled by a pilot mill simulating the typical thermo-mechanical process of heavy-wall seamless pipes (40 mm final thickness). All ingots were instrumented with thermocouples and the evolution of temperature during hot rolling was recorded. The hot rolled materials were quenched in stirred water and tempered under strictly controlled parameters (Table 1), being each piece instrumented by a thermocouple imbedded at mid-thickness. In order to assess the effect of PAGS and tempering temperature on microstructure and mechanical properties, a wide range of austenitizing and tempering conditions was used, which also included austenitizing temperatures higher than those usually applied on seamless pipes for promoting coarse AGS.

Table 1. Range of laboratory heat treatment conditions

	Min	Max
Austenitizing Temperature (°C)	920	1020
Cooling rate during quenching (°C/s)	10	25
Tempering Temperature (°C)	630	690

The Q&T materials were examined by light and scanning electron microscopy (LM & SEM). Microstructures were observed on sections after 2%-nital etching. Islands of high carbon martensite with retained austenite (MA constituent) were revealed by selective etching proposed by Colleluori (1983). The austenite grain boundaries were revealed by etching in a saturated aqueous picric acid solution containing a few drops of teepol and HCl. The average austenite grain size (AGS) was measured according with ASTM E112.

Packet and cell size were determined by Image Orientation Microscopy (OIM) technique using electron back-scattering diffraction (EBSD) pattern. By means of this technique, the surface of a crystalline material with low dislocation density can be scanned and in each point the orientation of the underlying grain can be determined in a fully automatic way. From these measurements some microstructural characteristics of the material can be estimated, e.g. misorientations and types of grain boundaries, crystallographic orientations, etc. It is of great importance to correctly assess the crystallographic grain size, because this parameter greatly influences the strength and the cleavage fracture resistance of ferritic steels. EBSD is a very accurate method to measure the grain size, even for microstructures as fine as tempered bainite and martensite. In addition, it provides information about much larger areas than those investigated by TEM.

Information on nature and size of fine precipitates was got by transmission electron microscopy with scanning attachment and high spatial resolution EDS microanalysis (TEM/STEM-EDS) using extraction replica.

Tensile and Charpy V-notch testing was conducted on transverse specimens. Charpy-V transition curves were determined together with the fracture appearance transition temperature (50% FATT).

3.2 Industrial Production and Pipe Qualification

Heavy-wall seamless pipes of medium diameter (OD = 219 to 323 mm) and WT = 30 to 44 mm were produced at Tenaris works by the seamless process, using the steel chemistry range and heat treatment conditions identified as promising by the metallurgical design. All pipes were manufactured according to specific customer requirements for production risers and flowlines. In particular, in addition to weldability requirements, in terms of carbon equivalent, $C_{eq\ (IIW)}$ and P_{cm} parameter, suitable tensile properties at room and high temperature shall be guaranteed (minimum yield strength at 130 °C = 448 MPa).

The characterization of selected pipes from the production was carried out by extensive metallography and mechanical testing, which included hardness measurements, longitudinal and transverse tensile testing, Charpy-V impact testing, crack tip opening displacement (CTOD) testing. CTOD was also performed in the HAZ of girth welds performed by GMAW. CTOD specimens were located at both the Transformed-HAZ (THAZ) and Visible-HAZ boundary (VHAZ). Post-test validity checks were carried out by specimen sectioning followed by fractographic and metallographic evaluation.

4. Results and Discussion

4.1 Strength-Toughness Combination

In order to attain the required yield strength of 448 MPa after tempering it is a pre-requisite to maintain the fraction of polygonal ferrite well below 30% (Anelli et al. (2004)).

The general pattern of strength/toughness properties as a function of (micro) alloy design, with reference to the same base composition (0.09C-1.3Mn-0.028Nb-0.05V) and quenching and tempering conditions, is reported in Figure 2.

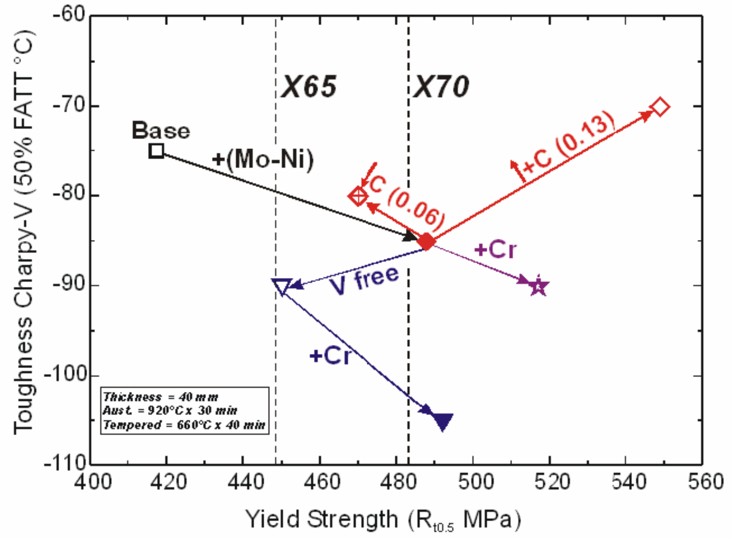


Figure 2. Toughness vs yield strength for various laboratory Q&T steels

Main findings are summarized below.

- The reduction of C content from 0.09% to 0.06% did not give substantial improvements in toughness although strength is slightly decreased.
- The increase of C content up to 0.13% gives strengthening (ΔYS = +60 MPa), but is detrimental to toughness and weldability.
- The addition of Mo and Ni (Mo-Ni-Nb-V) gives excellent strength/toughness combination, together with good field weldability: YS well above grade X65; 50%FATT as low as – 85°C; Ceq $_{(IIW)}$ = 0.38%.
- The V-free version (Mo-Ni-Nb) allows to reduce FATT, but at expense of strength (ΔYS = – 35 MPa).
- Addition of 0.22Cr produces further improvement in toughness (50% FATT below – 100°C) at expense of field weldability (Ceq = 0.42%).
- Mo-Ni-Nb-V-(Cr) steel resulted to be the most promising for the production of heavy-wall seamless pipes.

Further investigations were carried out on other laboratory steels. Starting from the base steel 0.085C-1.3Mn-0.15Mo-0.025Nb-0.05V, the following chemical elements were added single or in combination: 0.2Cr, 0.4Ni, 0.015Ti.

In this case, the effect of AGS was studied using austenitizing temperatures up to 1020 °C. The general pattern of strength/toughness properties as a function of (micro)-alloy design and PAGS for 40 mm WT Q&T materials produced by pilot plant is reported in Figure 3. Again, with reference to the reference chemical composition, for a given AGS of 10-12 μm, additions of Ni and Cr produce a strength increase, without significant effects on toughness (50% FATT below – 70°C). The V-free version (Mo-Ni-Nb steel) allows to reduce FATT, but at expense of strength.

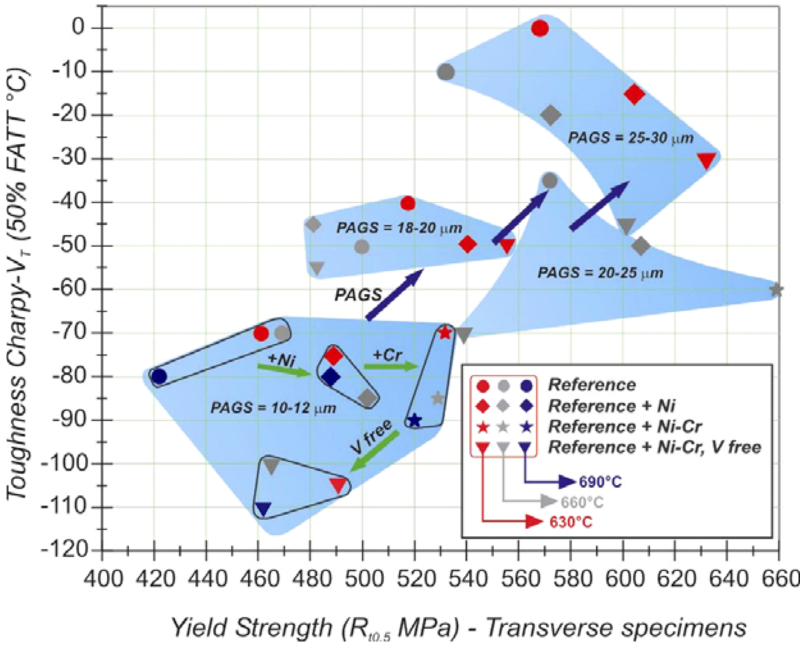
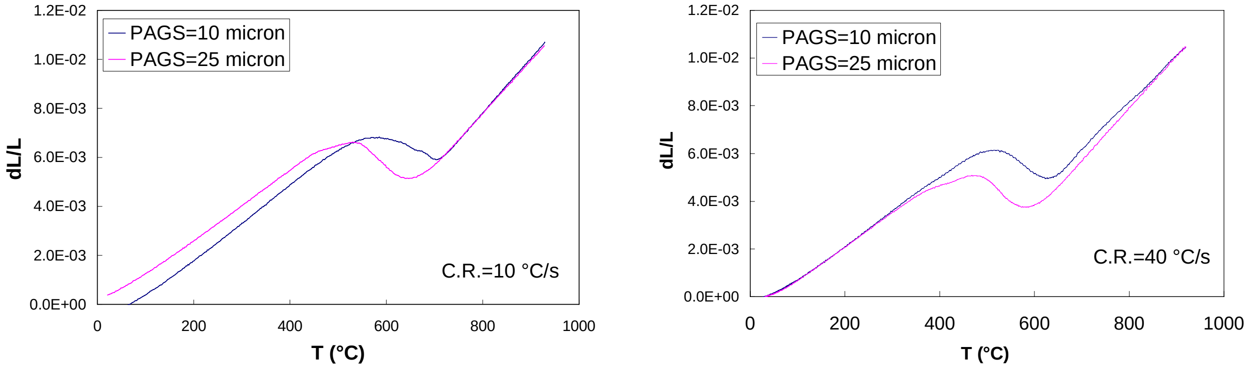


Figure 3. Strength/toughness combinations as a function of (micro)-alloy design and PAGS

Usually, the increase of tempering temperature from 630°C to 690°C leads to a decrease in YS of 25-45 MPa and a slight improvement of toughness in terms of 50% FATT (ΔFATT = – 10 to – 15 °C). For a given chemical composition, the coarsening of PAGS improves strength, but lowers toughness. The reasons for this behavior were investigated in terms of microstructural features which control strength and resistance to cleavage fracture.

4.2 Effect of PAGS on final microstructure and mechanical properties

The strengthening due to PAGS increase, for a given tempering temperature, was related to improved hardenability. Continuous cooling transformation (CCT) curves were determined by dilatometry for a given steel using different austenitizing conditions, corresponding to PAGS of 10 μm and 25 μm, respectively. Results from CCT curves showed a strong effect of PAGS on hardenability. For instance, a structure of 9%M-52%B-39%F formed at CR = 40 °C/s when PAGS = 10 μm was modified to 38%M-57%B-5%F in the case of 25 μm PAGS. In addition, the dilatometric curves reported in Figure 4, and the corresponding transformation temperatures summarized in Table 2, show that larger PAGS lowers the transformation temperature range. This means higher dislocation density of the as-quenched microstructure. PAGS can influence strength/toughness combination acting on packet/cell sizes. In fact, high-angle misorientation grains (packets) and low-angle misorientation grains (cells or sub-grains) are the microstructural features affecting toughness and strength, respectively, as reported by Brozzo et al. (1977) for bainitic steels. Their dependence on PAGS was determined by means of OIM for selected materials (Figure 5).



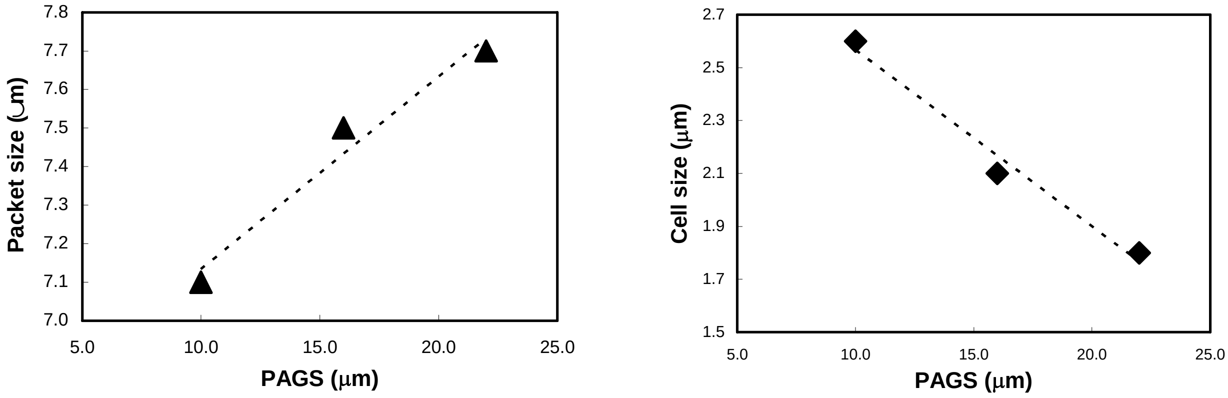
a

b

Figure 4. Effect of PAGS on length change of dilatometric specimens during cooling: a) CR = 10 °C/s; b) CR = 40 °C/s)

Table 2. Effect of PAGS and CR on transformation temperatures

PAGS (μm)	**10 °C/s**		**40 °C/s**	
	Start	**Finish**	**Start**	**Finish**
10	724	434	706	425
25	657	386	630	310



a **b**

Figure 5. Effect of PAGS on packet (a) and cell (b) sizes

Increasing PAGS from 10 μm to 23 μm, increases the packet size from 7 to 8 μm. This leads to a decrease in toughness, *i.e.* higher ductile-brittle transition temperatures (50% FATT), even when the values were normalized to a same strength level (Table 3). Finer cell sizes were found in the material with the largest austenitic grain (Figure 5b), hence with the highest volume fractions of bainite-martensite, justifying the strengthening.

Table 3. Strength-toughness combination of Q&T steels with different microstructural parameters

dpacket	dcell	YS	FATT	ΔFATTnormalized
(μm)	(μm)	(MPa)	(°C)	(°C)
7.1	2.6	481	– 55	– 56
7.5	2.1	482	– 45	– 46
7.7	1.8	601	– 35	0

This can be interpreted in the light of classical theoretical model for cleavage fracture, dictating that the critical stage for cleavage cracking is the propagation of a small crack originated in a single packet to the adjacent one. This means that only the high-angle boundaries are effective barriers to crack propagation and that the smaller is the packet the smaller is the incipient crack, that is the smaller is the possibility for such crack to reach the "critical" size for propagation.

4.3 Precipitation and PAGS Control

Due to the influence of PAGS on strength/toughness combination, it is important to investigate the effect of micro-alloying on precipitation and inhibition of austenite grain growth. In multi-micro-alloyed steels, carbides and nitrides of Ti, Nb and V show extensive mutual solubilities which arises from the fact that they have the same cubic crystal structure and have very similar lattice parameters.

As-quenched Nb-V steels exhibited, in addition to rare coarse (200-300 nm) precipitates, also very fine precipitates. These Nb rich (Nb> 92%; V < 7%; Mo< 1%) particles, already present in the as-rolled material, remained un-dissolved during austenitizing and exert a very effective inhibition of grain coarsening.

The addition of small amounts of Ti modified the size distribution of fine particles, which resulted slightly coarse, but still effective in controlling austenite grain growth (Table 4). Only for temperatures higher than 1000 °C, due to the dissolution of carbides, the average PAGS was greater than 20 μm.

Table 4. Micro-alloying effect on precipitation and PAGS after austenitizing at 900-950 °C

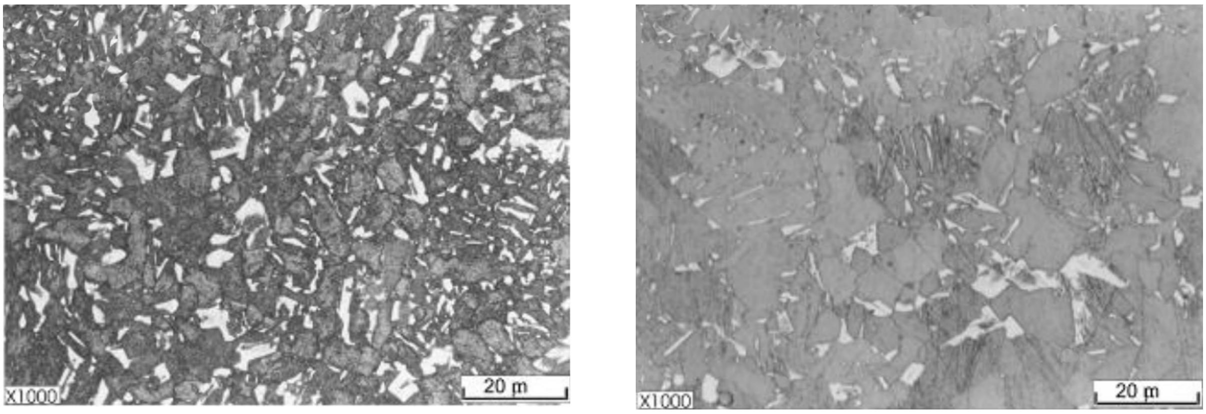
	Precipitate mean size (nm)	PAGS (μm)
Ti-free	17.4	10-13

steel		
Ti steel	25.5	15-18

4.4 Industrial Production

The industrial production confirmed the effect of main process parameters and metallurgical factors on microstructure and strength-toughness combination, as outlined by the laboratory experiments, and allowed to identify the actions for a fine tuning to develop a good combination of strength and toughness.

In the case of coarse austenite grains and relatively low cooling rates during quenching (*e.g.* low water flow and wall thickness greater than 38 mm) the volume fraction of MA constituent can increase and relatively coarse MA islands appear (Figure 6a).



a **b**

Figure 6. Distributions of MA islands revealed by selective etching in quenched pipes; a) coarse PAGS and low cooling rates and; b) effective quenching and more homogeneous and refined PAGS

These islands, to be transformed into a mixture of ferrite and carbides, require higher temperatures and longer times during tempering. In addition, an aggregate of cementite particles is expected along grain boundaries, where large MA islands were present, after tempering. When the PAGS is fine and the quenching is effective, *i.e.* the volume fraction of bainite is greater than 80%, the MA constituent is finely distributed as small islands between the bainite laths (Figure 6b). Pipes after Q&T can present a high number of cementite particles which decorate the grain boundaries. Sometimes, residuals of MA islands can be still recognized when very low tempering temperatures are used. All hardness tests on Q&T pipes were below 248 HV_{10}. The mechanical properties of various industrial materials in terms of 50% FATT and yield strength are summarized in Figure 7.

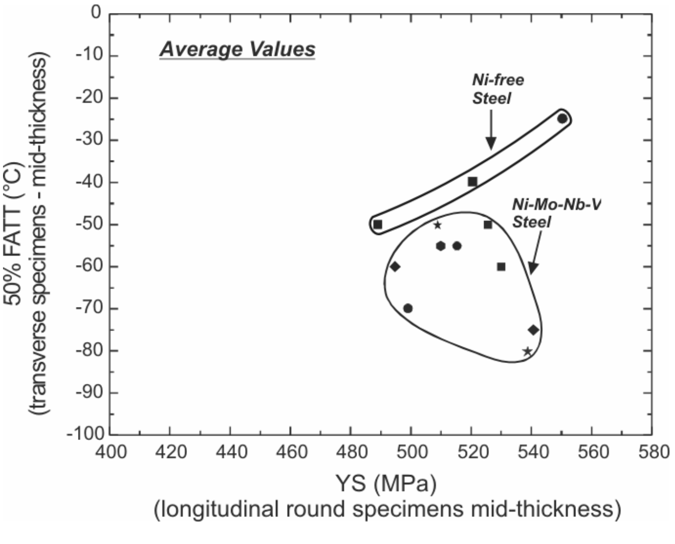


Figure 7. Toughness vs yield strength for heavy wall seamless pipes

The materials produced using the Mo-Ni-Cr-Nb-V steel, have significantly improved toughness for a given yield strength level between 460 and 530 MPa, compared to the conventional chemistry without Ni. The productions indicate that suitable toughness levels (*i.e.* 50% FATT < – 50°C) have been achieved. Also high CTOD values at – 10 °C (> 1.1 mm) were measured on the Q&T seamless pipes. Best results were attributed to the following aspects:

1. Strict control of process parameters during heating in order to develop uniform and small PAGS;
2. More effective quenching to promote higher volume fractions of bainite and a more refined final microstructure;
3. Fine tuning of Mo, Cr, V and Ni additions.

Suitable strength levels of pipes for flowlines and production risers shall be achieved also at 130 °C because fluids at high temperatures are processed. The yield strength of Q&T heavy wall pipes was determined at testing temperature up to 200 °C. As expected, there was a drop in proof strength at 50 to 100 °C, compared with the room temperature value. There was little further change as the temperature was increased to 150°C. The yield strength remained well above the minimum acceptable value for all the temperatures considered.

A few pipes were girth welded by GMAW using low (0.6 kJ/mm) and high (3.0 kJ/mm) heat inputs. The CTOD results at 4 °C were quite good both for the THAZ (CGHAZ), with values of 0.6 – 1.0 mm and the VHAZ with values of 1 - 1.5 mm. At – 10 °C, CTOD remained always greater than 0.3 mm.

5. Conclusions

New chemistries and optimized Q&T conditions were identified for the production of seamless pipes for both flowlines and risers with WT up to 44 mm. Main conclusions are:

- The as-quenched microstructure plays a primary role. The best toughness values are related to a predominantly bainitic microstructure after quenching (ferrite < 30%) combined with a homogeneous and fine distribution of MA constituent. This is promoted through the control of austenite grain growth (PAGS < 20 μm) during the heating stage and an effective quenching.
- Small cells (< 2.5 μm) and packets (< 7.5 μm) are the key factors to develop adequate strength-toughness combination (YS=480-540 MPa, 50% FATT< -50 °C).
- The tempering temperature has a secondary role. However, higher tempering temperature leads always to a slightly improved toughness in the case of coarse MA islands.
- The Mo-Ni-Cr-Nb-V alloy system showed the best combination of strength-toughness.
- The CTOD results in the HAZ of GMAW girth joints indicated good weldability.

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